

**Fitting Vapor Pressure - Temperature Data:
Simplicity and Unintended Consequences**

M. Frenkel^{a,*}, G. A. Iglesias-Silva^c, S. M. Mannan^b and K. R. Hall^{a,b}

^aThermodynamics Research Center, Texas A&M University System,
College Station, TX 77843-3111, USA

^bChemical Engineering Department, Texas A&M University,
College Station, TX 77843-3122, USA

^cDepartamento de Ingeniería Química, Instituto Tecnológico de Celaya,
Celaya, Guanajuato, CP 38010, Mexico

*Corresponding author

Abstract

The (1, 1.5, 3, 6) Wagner vapor pressure equation has gained acceptance in a variety of applications, *e.g.* in various software packages designed to ‘simulate’ chemical engineering processes. While this equation can fit vapor pressure data over the entire temperature range including the vicinity of the critical point, indiscriminate use of this equation can lead to substantial extrapolation errors and erroneous enthalpies of vaporization. Several examples of vapor pressure fits compare results obtained from the (1, 1.5, 3, 6) Wagner equation with other equations having constraints at the lower and higher pressure limits.

Introduction

Vapor pressures of pure chemicals are among the most important thermodynamic properties used for chemical process design, separation technology, transportation and storage of chemicals, environmental and safety controls, and development of equations of state. Vapor pressure equations simplify extrapolation and interpolation of data. Process simulation software packages use these equations to derive values of related thermophysical properties, such as the enthalpy of vaporization. Generally, vapor pressure equations result from integration of the Clausius-Clapeyron equation and/or expansion about the critical point. Normally, fitting equations contain several adjustable parameters obtained from experimental data. Some of these empirical equations (*Antoine* [1], *Cox*) with adjustable parameters are accurate at low temperatures but do not fit the data adequately near the critical point. Reid *et al.* [2] compile complex and accurate equations. Wagner [3] has proposed an alternative procedure to provide a high quality fit for vapor pressure data over the entire temperature range. This procedure, first formulated for nitrogen and argon, requires a stepwise selection of the equation terms. Recently, a particular form developed using this approach, the (1, 1.5, 3, 6) Wagner equation (W36), has become popular for numerous applications involving various classes of chemical compounds [4,5]. We should note that Wagner uses his method to produce an accurate equation for each compound rather than proposing a single form for all compounds. In this paper, we analyze whether indiscriminate use of this equation assures an adequate extrapolation of vapor pressure data and calculation of the enthalpy of vaporization. This question is of particular concern when

fitting data of varying quality reported by multiple sources. We also compare results obtained using W36 with those obtained using equations constrained at the lower and upper vapor pressure limits.

Vapor Pressure Equations

Wagner [3] has demonstrated that Eq 1 can represent the vapor pressures of argon and nitrogen accurately:

$$\ln\left(\frac{P}{P_C}\right) = \frac{(a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6)}{1 - \tau} \quad (1)$$

where $\tau = 1 - T / T_C$ and P_C and T_C are the critical pressure and temperature, respectively.

Eq (1) is W36 and has four adjustable parameters (a , b , c , and d).

Iglesias-Silva *et al.* [6] use the asymptotic behavior from the Clausius-Clapeyron equation near the triple point and asymptotic scaling-law behavior in the critical region to obtain

$$p^N = p_0^N + p_\infty^N \quad (2)$$

where the asymptotic behavior at low temperatures is

$$p_0 = a_0 + a_1 (1 + a_3 t)^{b_0 / R} \exp \left[\frac{b_0 / R - a_2}{1 + a_3 t} \right] \quad (3)$$

with

$$a_0 = 1 - P_t / (P_C - P_t)$$

$$a_1 = (1 - a_0) \exp [a_2 - b_0 / R]$$

$$a_2 = b_1 / RT_t$$

and

$$a_3 = (T_C - T_t) / T_t.$$

For the asymptotic behavior near the critical point,

$$p_\infty = 2 - a_4(1 - t) + a_5(1 - t)^{1.8} + a_6(1 - t)^3 + a_7(1 - t)^4 \quad (4)$$

with

$$a_5 = -0.11599104 + 0.29506258a_4^2 - 0.00021222a_4^5$$

$$a_6 = -0.01546028 + 0.08978160a_4^2 - 0.05322199a_4^3$$

$$a_7 = 0.05725757 - 0.06817687a_4 + 0.00047188a_4^5.$$

In Eq 2, $N = 87(T_i / T_C)$ and the adjustable parameters are a_4 , b_0 , and b_1 . The dimensionless temperature and pressure are:

$$p = 1 + \frac{P - P_t}{P_C - P_t}$$

$$t = \frac{T - T_t}{T_C - T_t}.$$

Vapor pressures provide enthalpies of vaporization through the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T(V^V - V^L)} \quad (5)$$

where ΔH is the enthalpy of vaporization, V^V is the vapor volume and V^L is the liquid volume. It is clear from Eq 5 that inadequate representation of the P - T dependence might lead to serious errors in calculated enthalpies of vaporization.

In summary, the principal difference between Eq 1 and Eq 2 is that Eq.1 is constrained at the critical point while Eq. (2) is constrained at the triple and critical points. To analyze various cases related to vapor pressure fits using Eqs 1 and 2, we have extracted several experimental vapor pressure-temperature data sets from the TRC SOURCE database [17].

Results

We have extracted vapor pressure data for methane and propylbenzene to compare the results obtained using Eqs 1 and 2. Our first test uses experimental vapor pressure data for methane reported by Kleinrahm and Wagner [7] to test the extrapolation capabilities of Eqs. 1 and 2. These experimental data are of extremely high quality. For the purpose of the analysis, we consider four different cases: in Case I, we use only experimental measurements from 150 K to the critical point; in Case II, we take measurements from 162 K up to the critical point; in case III, we use data from 165 K to T_C ; and in case IV, we fit the equation to data from 170 K up to the critical point. It is important to note that all these cases are difficult for accurate fitting by any vapor pressure equation because in the best case we are using data that covers a reduced temperature range from 0.79 to 1.00. In all cases, the parameters are valid with a 95 % confidence interval. The characteristic parameters appear in Table I together with the asymptotic error.

Figures 1 and 2 illustrate the extrapolation performance for both equations. We have used a log-linear plot as suggested by Holste *et al.* [8] to keep all the residual values on a single, easy-to-read plot. This type of plot is useful when significant differences exist

among the residual values. As shown in Figure 1, the best extrapolation for Eq. 1 occurs in Case I, in which the percentage deviation of the equation from experimental data ranges up to 100 %. In all other cases, the extrapolation is worse and cannot be considered adequate at low pressures. On the other hand, for a doubly-constrained equation, such as Eq. 2, the deviation ranges from 0.5 % in Case I at low pressures to 10% at 120 K in Case IV.

Because the slope of the temperature-pressure dependence has direct impact on the value of the enthalpy of vaporization, it is also interesting to compare the values of the first and second derivatives resulting from Eqs 1 and 2. Figures 3 and 4 show the values of the first derivative as a function of temperature obtained from Eqs 1 and 2, respectively (the parameters of the equations appear in Table 1). For Eq 1 in Case I, the behavior of the first derivative is correct, but in the other three cases the numerical values of the first derivative changes from positive at higher temperatures to negative at lower temperatures. This behavior indicates that the vapor pressure-temperature dependence might have local minima and/or maxima as illustrated by Figure 5 for Eq 1 in Case III. A negative slope would also produce a negative value for the enthalpy of vaporization. Indeed, taking the first derivative of the Eq 1 with respect to temperature leads to an extremum at:

$$\frac{df}{dT_r} = \frac{f}{T_r} \quad (6)$$

with

$$f = a\tau + b\tau^{1.5} + c\tau^3 + d\tau^6$$

and

$$\frac{df}{dT_r} = -(a + 1.5b\tau^{0.5} + 3c\tau^2 + 6d\tau^5).$$

For the second derivative to change sign, the first derivative must be

$$\frac{dP}{dT_r} = \frac{P}{T_r} \left[1 \pm \sqrt{1 + T_r \frac{d^2f}{dT_r^2}} \right]. \quad (7)$$

This analysis shows that the particular results for extrapolating these experimental data Eq 1 are not accidental but result from the nature of this equation.

We have also extracted the experimental vapor pressure data reported for propylbenzene in a number of sources [9-16]. Here, we have a situation in which substantial disagreement exists among various data sets. In particular, one data set [9] does not agree with the others (a typical situation for data evaluation and process simulation). We have fit both equations to all the data using unweighted least squares. Figures 6 and 7 are the residual plots obtained from those fits. It is apparent that both equations predict the vapor pressure behavior with the same accuracy. However, when we plot the first derivative of the pressure with respect to temperature from Eqs 1 and 2, the derivative from Eq 1 is negative below 260 K corresponding to negative enthalpies of vaporization. When we exclude the data of Woringer [9] from the fit, the first derivative from both equations has

the correct behavior, as shown in Figure 8. The change in sign in the first derivative corresponds to a minimum in a pressure *versus* temperature plot as shown in Figure 9. Figure 10 presents the second derivative of the vapor pressure with respect to temperature as a function of temperature. Obviously, the curve corresponding to Eq 1 does not have proper shape when fitting all the data, but proper behavior does result when the data reported in [9] are excluded. The behavior of the second derivative using Eq 2 in both cases (although not the same) is adequate for calculation of thermodynamic properties.

Conclusions

We have shown that the W36 vapor pressure equation can present anomalous behavior when used for extrapolation. Also, the equation can lead to a minimum value on the vapor pressure - temperature curve when fitting data sets of different quality to determine the characteristic parameters. In both cases, negative values of the enthalpy of vaporization can result using the Clausius-Clapeyron equation. That information should be considered when using Eq 1 in data evaluation and computer simulation software packages. Ignoring this effect might lead to serious errors when extrapolating vapor pressure data or calculating other properties based upon these data. Equations constrained at both the critical and triple points, such as Eq 2, seem to avoid this problem.

Acknowledgments

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References

- [1] C. Antoine, *Comm. Roy. Acad. Sci.*, 107 (1888) 681.
- [2] Reid, R. C., Prausnitz, J. M., Poling, B. E.; *The Properties of Gases and Liquids*, 4th Ed., McGraw-Hill, New York, 1987.
- [3] Wagner, W.; *Cryogenics*, 13 (1973) 470-482.
- [4] Ambrose D., Patel, N.C.; *J. Chem. Thermodyn.*, 16 (1984) 459-468.
- [5] McGarry, J.; *Ind. Eng. Chem. Process Des. Dev.*, 22 (1983) 313-322.
- [6] Iglesias-Silva, G. A., Holste, J. C., Eubank, P. T., Marsh, K. N., Hall, K. R.; *AIChE J.*, 33 (1987) 1550-1556.
- [7] Kleinrahm R., Wagner, W.; *J. Chem. Thermodyn.*, 18 (1986) 739-760.
- [8] Holste, J. C., Hall, K. R., Iglesias-Silva, G. A.; *AIChE J.*, 42 (1996) 296-297.
- [9] Woringer, B.; *Z. Phys. Chem. Stoechiom. Verwandtschaftsl.*, 34 (1900) 257-289.
- [10] Linder, E. G.; *J. Phys. Chem.*, 35 (1931) 531-535.
- [11] Willingham, C. B., Taylor, W. J., Pignocco, J. M., Rossini, F. D.; *J. Res. Natl. Bur. Stand.*, 35, (1945) 219-244.
- [12] Forziati, A. F., Norris, W. R., Rossini, F. D.; *J. Res. Natl. Bur. Stand.*, 43 (1949) 555-563
- [13] Funk, E. W., Chai, F-C., Prausnitz, J. M.; *J. Chem. Eng. Data*, 17 (1972) 24-27.
- [14] Gierycz, P., Rogalski, M., Malanowski, S.; *J. Fluid Phase Equilibria*, 22 (1985) 107-122.
- [15] Rogalski, M.; *J. Chem. Thermodyn.*, 17 (1985) 921-926.

[16] Paul, H-I., Krug, J., Knapp, H.; *Thermochim. Acta*, 108 (1986) 9-27.

[17] *Documentation for the TRC SOURCE Database*, TRC: College Station, 2000.

Table 1. Characteristic Parameters used in Eqs 1 and 2 for Methane.

	Equation 1				Equation 2		
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	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>b</i> ₀	<i>b</i> ₁	<i>a</i> ₄
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Case I

Estimate	6.022964	1.246170	1.193417	10.67552	18.38270	8784.489	3.162660
Error	0.000640	0.002933	0.028237	1.493991	0.308375	7.492808	0.000352

Case II

Estimate	6.025656	1.261612	1.446202	42.70235	21.89247	8881.393	3.161010
Error	0.000456	0.002427	0.037070	5.129415	1.144515	31.78003	0.000523

Case III

Estimate	6.026461	1.266767	1.563544	70.98807	26.00556	9002.085	3.159963
Error	0.000396	0.002251	0.042215	8.905518	1.951981	56.90668	0.000531

Case IV

Estimate	6.028119	1.278880	1.988392	352.8160	34.82770	9272.515	3.158766
Error	0.000239	0.001733	0.067666	62.95676	3.743513	114.7844	0.000482

Figure Captions

Figure 1. Percentage deviation of Eq 1 from Experimental Data of Methane from Kleinrahm and Wagner [7]. O, Case I; ▽, Case II; □, Case III; Δ, Case IV.

Figure 2. Percentage deviation of Eq 2 from Experimental Data of Methane from Kleinrahm and Wagner [7]. O, Case I; ▽, Case II; □, Case III; Δ, Case IV.

Figure 3. Temperature Behavior of the First Derivative of the Pressure from Eq 1: Solid Line, Case I; Long Dash Line, Case II; Medium Dash Line, Case III; Short Dash Line, Case IV.

Figure 4. Temperature Behavior of the First Derivative of the Pressure from Eq 2: Solid Line, Case I; Long Dash Line, Case II; Medium Dash Line, Case III; Short Dash Line, Case IV.

Figure 5. Pressure-Temperature Behavior of Methane from Eq 1 for Case III.

Figure 6. Percentage deviation of Eq 1 from Experimental Data of Propylbenzene: O, Woringer [9]; ▽, Linder [10]; □, Willingham *et al.* [11]; Δ, Forziati *et al.* [12]; ◇, Funk *et al.* [13]; ●, Rogalski [15]; ▼, Paul *et al.* [16]; and ■, Gierycz, *et al.* [14].

Figure 7. Percentage deviation of Eq 2 from Experimental Data of Propylbenzene: O, Woringer [9]; ∇ , Linder [10]; \square , Willingham *et al.* [11]; Δ , Forziati *et al.* [12]; \diamond , Funk *et al.* [13]; \bullet , Rogalski [15]; \blacktriangledown , Paul *et al.* [16]; and \blacksquare , Gierycz, *et al.* [14].

Figure 8. Temperature Behavior of the First Derivative of the Pressure for both Equations: Solid Line, Eq 2 including all the data in the fit; Long Dash Line, Eq 2 excluding Woringer Data [9]; Medium Dash Line, Eq 1 including all the Data in the Fit; Short Dash Line, Eq 1 excluding Woringer Data [9].

Figure 9. Pressure-Temperature Behavior of Propylbenzene: $--$, Eq 1 and $---$, Eq 2.

Figure 10. Temperature Behavior of the Second Derivative of the Pressure from both Equations: Solid Line, Eq 2 including all the data in the fit; Long Dash Line, Eq 2 excluding Woringer Data [9]; Medium Dash Line, Eq 1 including all the Data in the Fit; Short Dash Line, Eq 1 excluding Woringer Data [9].

Figure 1

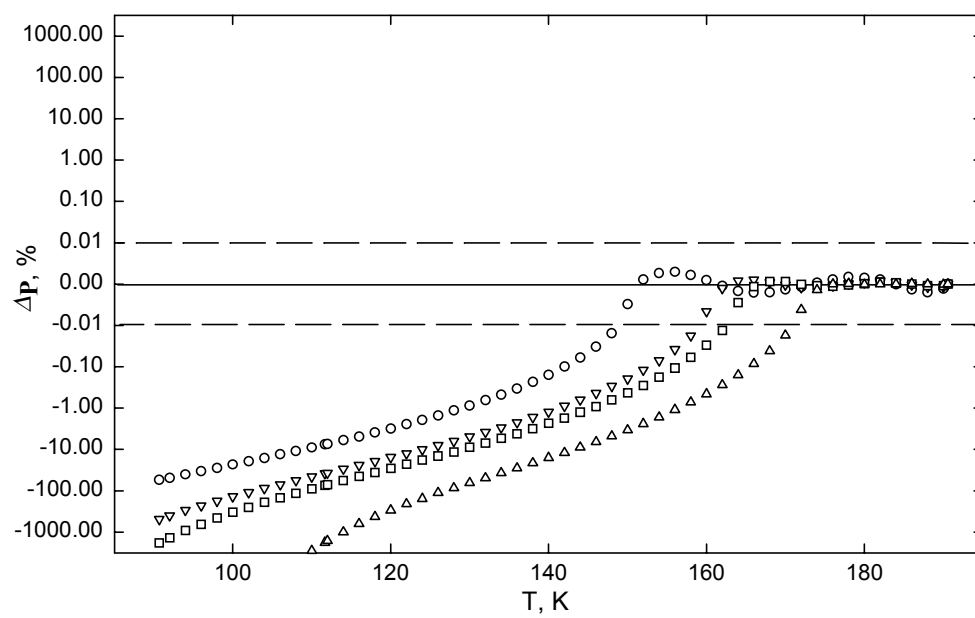


Figure 2

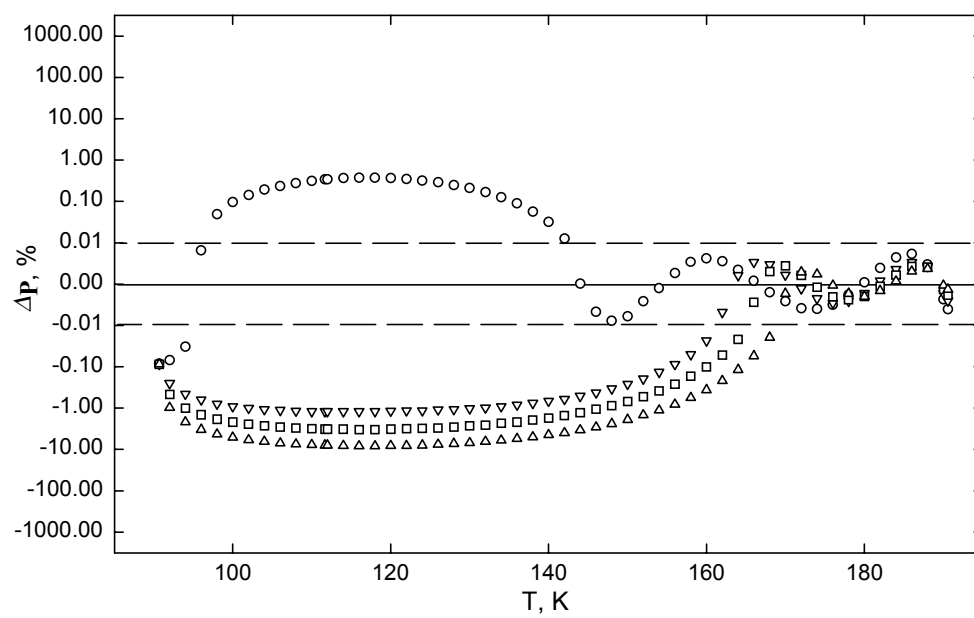


Figure 3

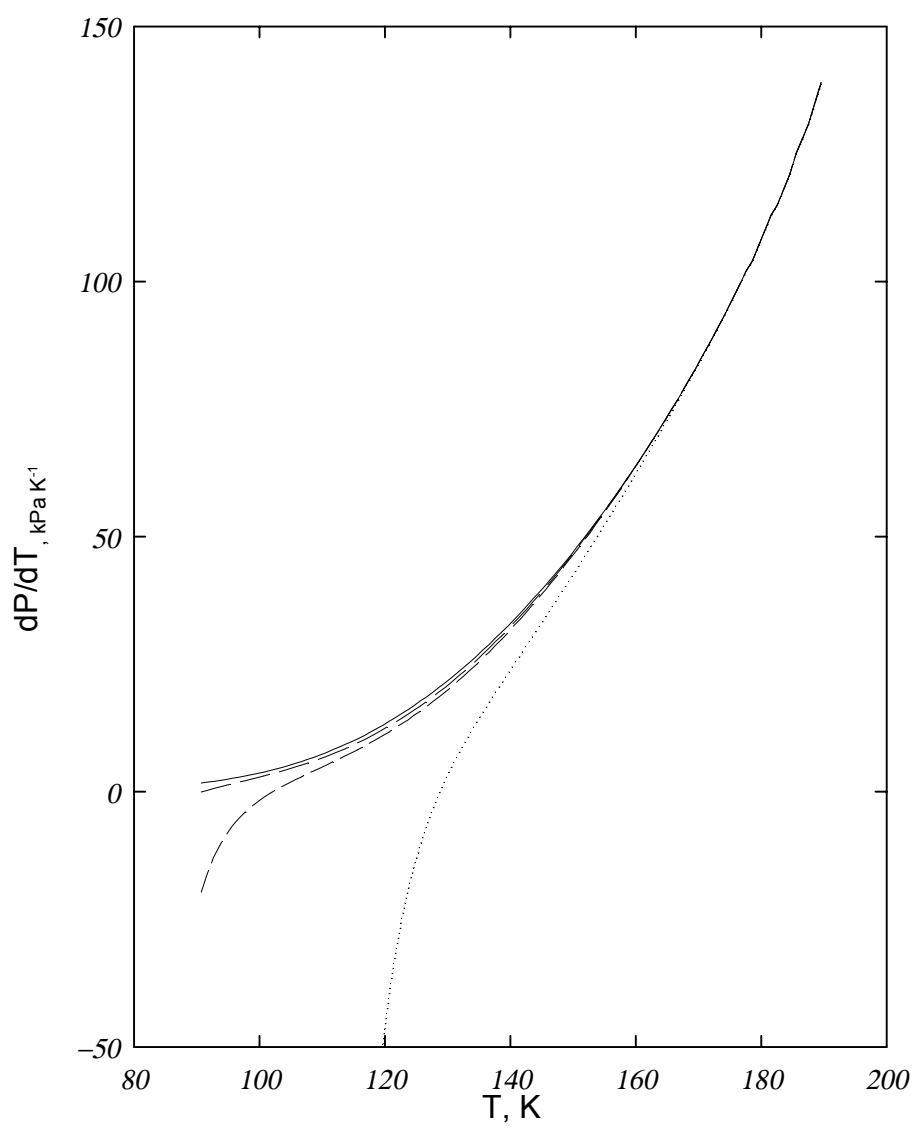


Figure 4

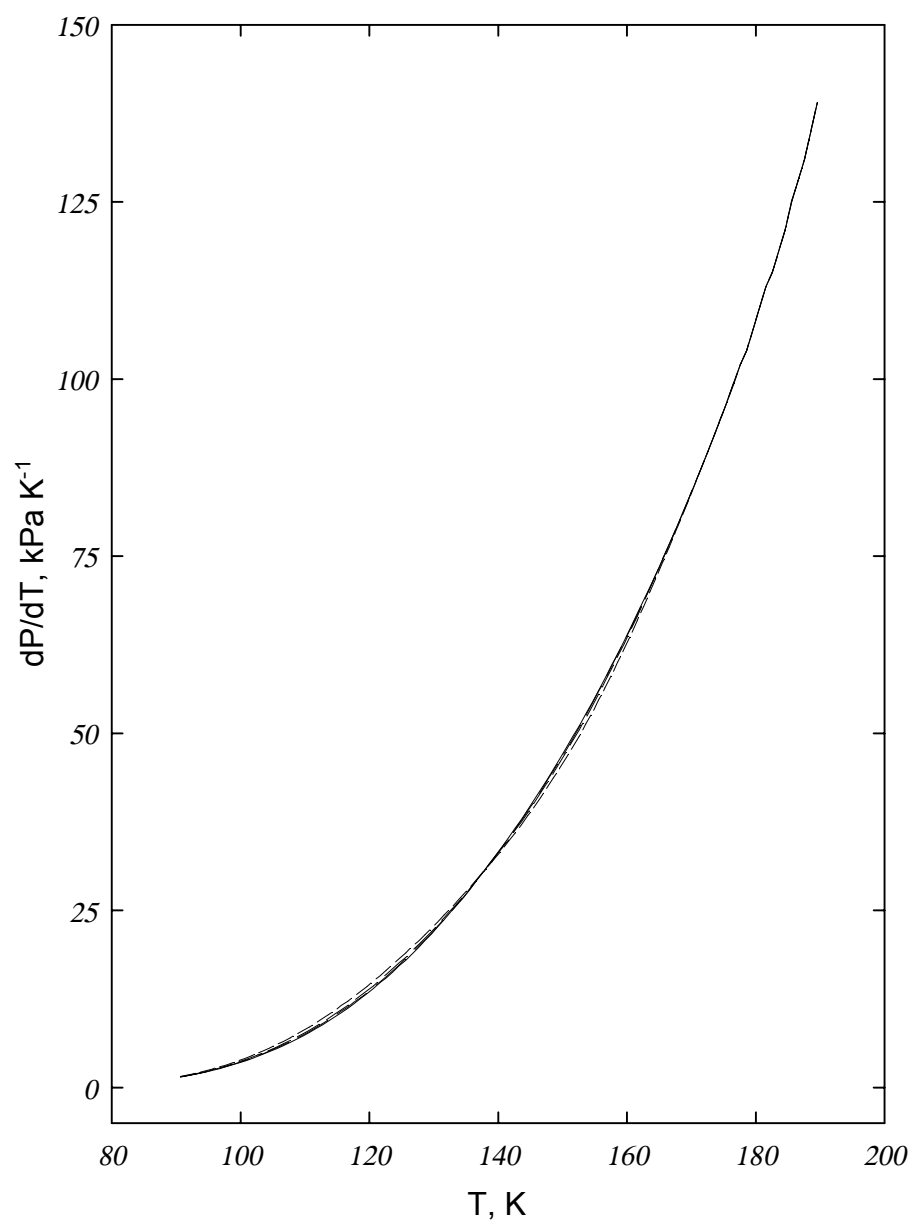


Figure 5

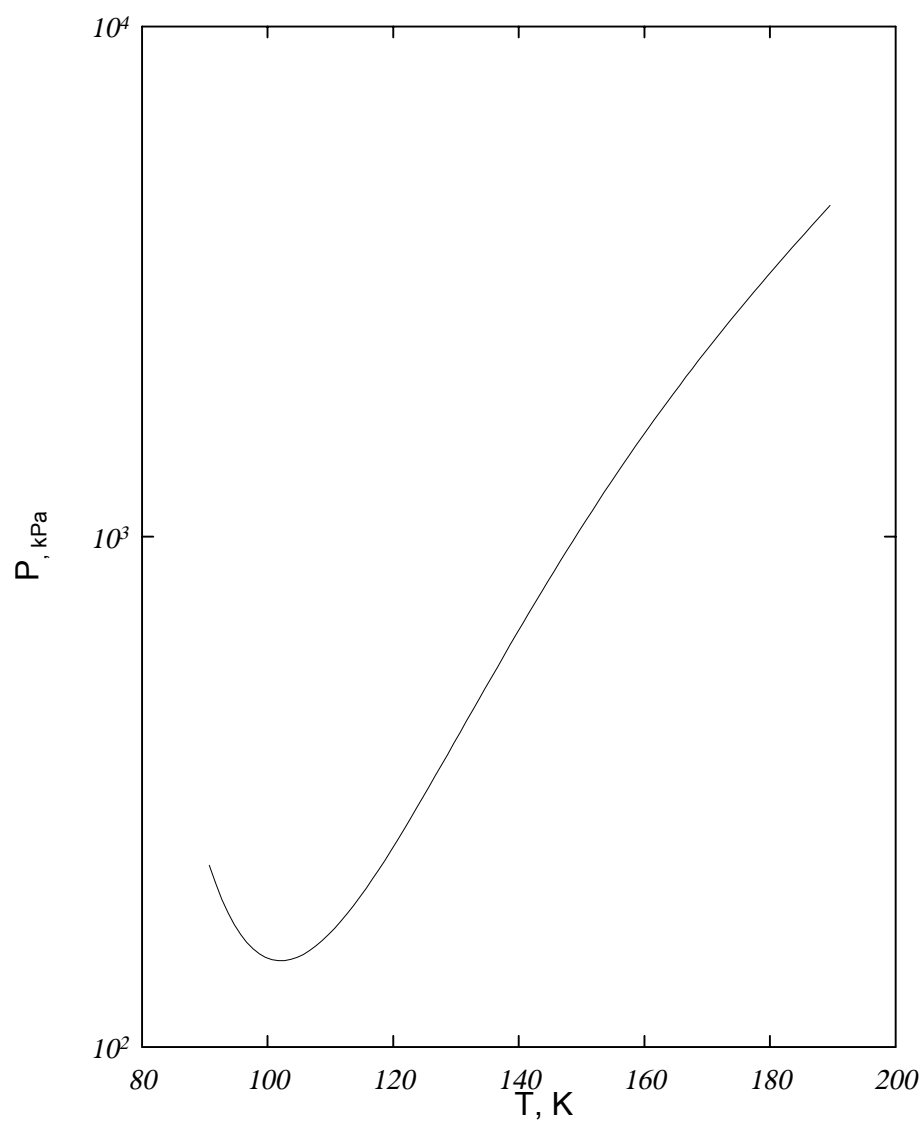


Figure 6

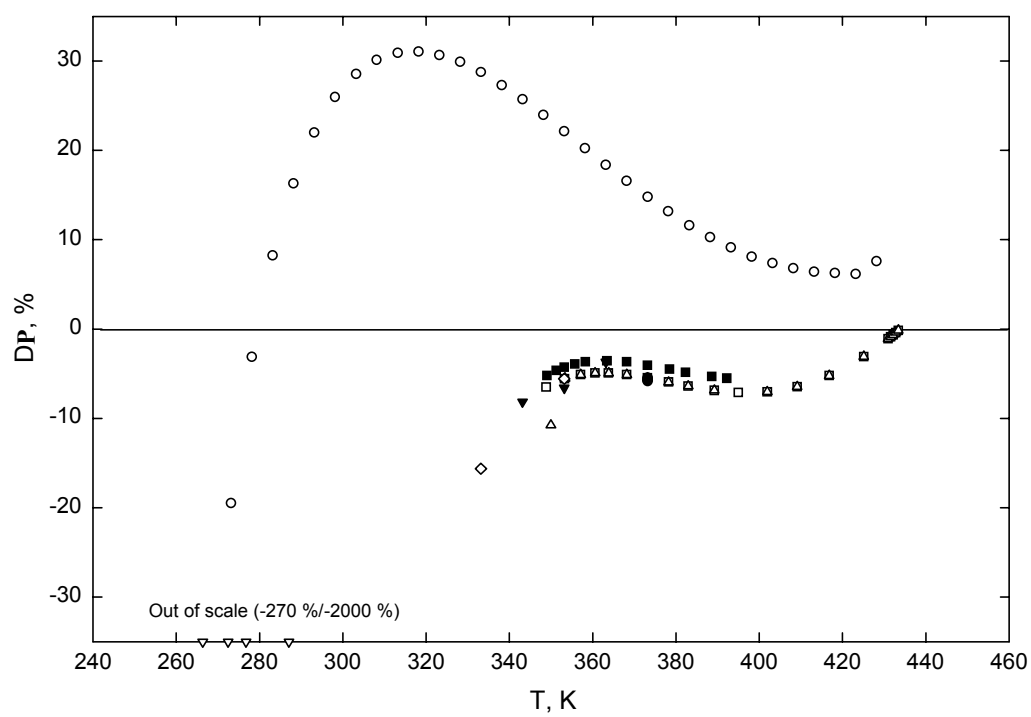


Figure 7

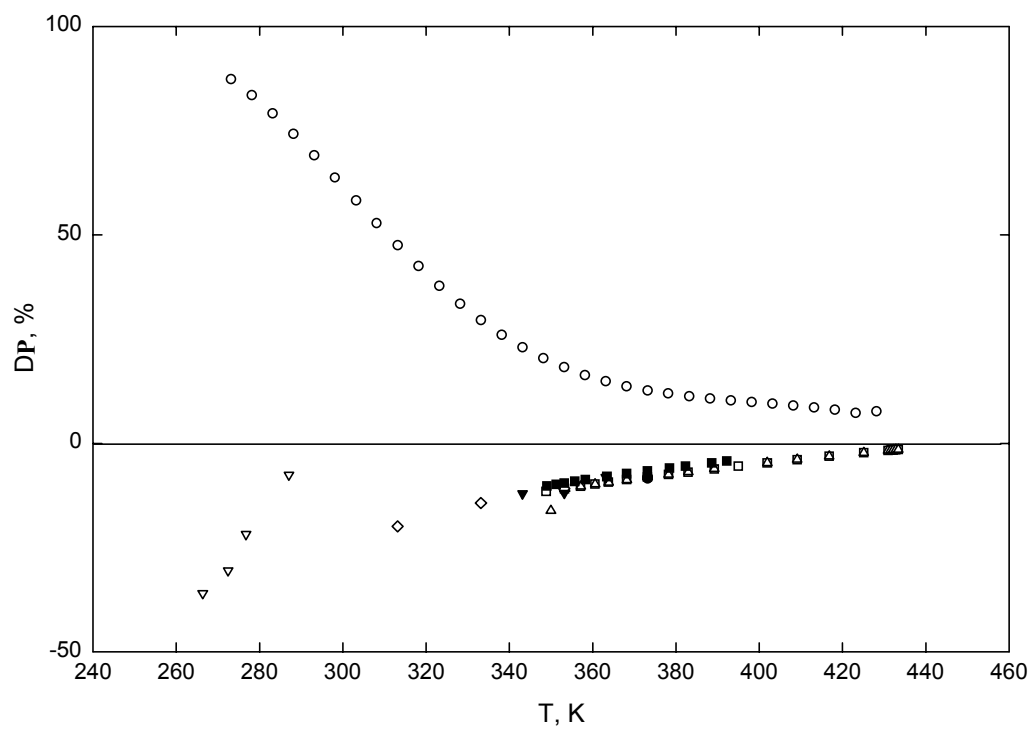


Figure 8

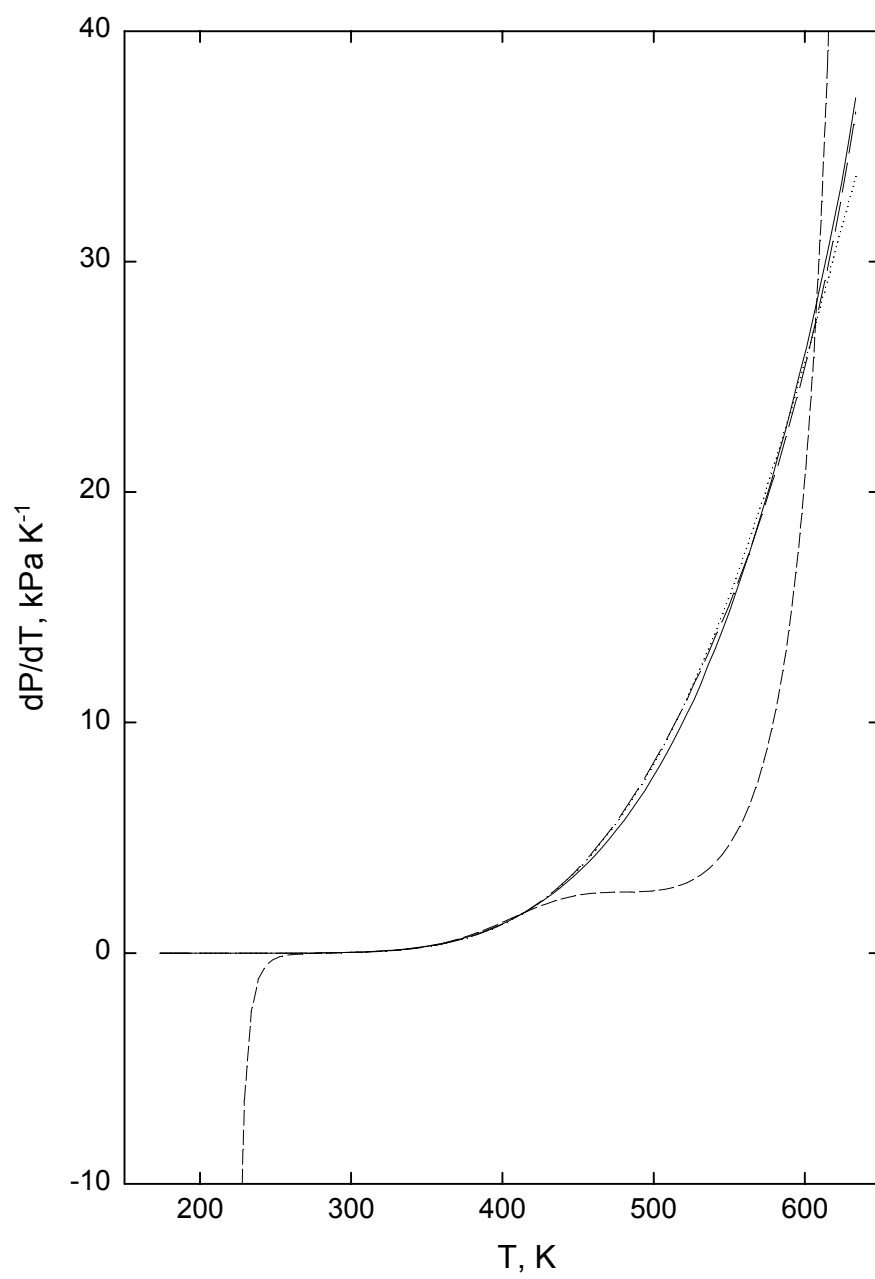


Figure 9

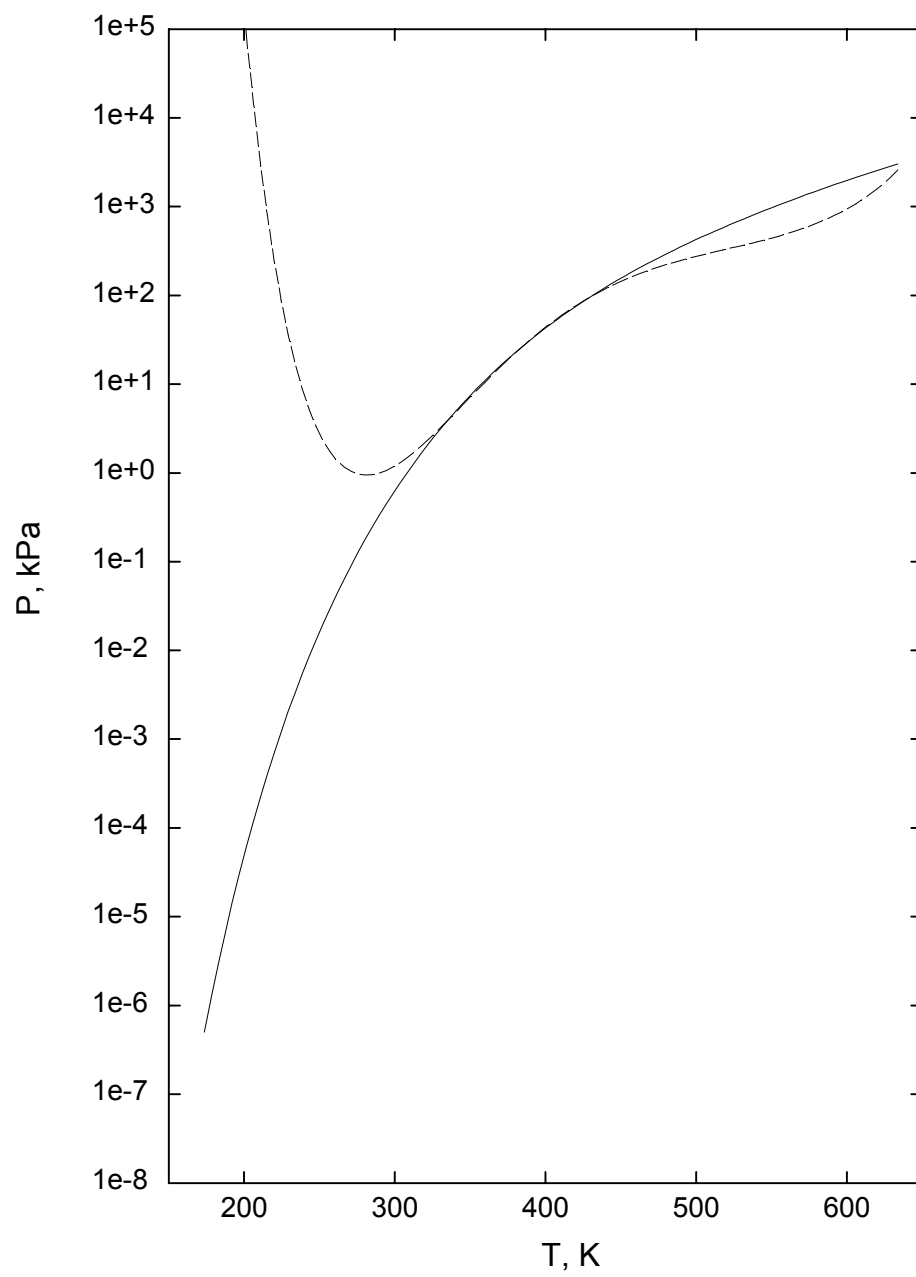


Figure 10

